

Experiment 22

IODINE CLOCK - THE INTEGRATED RATE LAW

Objective

The purpose of this experiment is using the graphic method (integrated rate law) to investigate the reaction order of the reaction between persulfate ($\text{S}_2\text{O}_8^{2-}$) and iodide (I^-) ions. The activation energy and catalytic effect are also studied.

Lab techniques

- Operating graduated pipet, dispenser, and timer.

Introduction

I. The reaction rate of persulfate and iodide ions

In experiment 8, we have been studied the rate law of the reaction between persulfate ($\text{S}_2\text{O}_8^{2-}$) and iodide (I^-) ions (22-1) by initial rate method. To determine the initial rate of reaction, we add a known amount of thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) to the solution to act as a limiting reagent. Thiosulfate ions can react with iodine molecules (I_2), one of the products of the previous reaction, as shown in equation 22-2. The reaction between $\text{S}_2\text{O}_3^{2-}$ and I_2 is extremely fast; hence, the I_2 produced in reaction 22-2 is immediately consumed. When $\text{S}_2\text{O}_3^{2-}$ is present in the solution, I_2 cannot exist concurrently. But once $\text{S}_2\text{O}_3^{2-}$ is consumed completely, I_2 can react with I^- to form I_3^- , which will form a blue-black complex with the starch indicator added to the reaction mixture. By recording the time taken (Δt) for the blue-black color to appear and using the stoichiometric relationship between $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_2\text{O}_8^{2-}$ (22-3), we can determine the concentration of $\text{S}_2\text{O}_8^{2-}$ at various time (Δt) as reaction proceeds.



II. The integrated rate law

In this experiment we will use a graphic method (integrated rate law) to investigate the reaction order of $\text{S}_2\text{O}_8^{2-}$. We will proceed by first looking at a reaction involving a single reactant, $\text{A} \rightarrow \text{P}$, the integrated rate laws are developed as followings.

1. Zero order reaction

If the reaction is zero order with respect to A (rate is independent of [A]), then the rate law equation is

$$\text{rate} = \frac{-d[A]}{dt} = k \quad (22-4)$$

Integrating the equation, then

$$[A] = -kt + [A]_0 \quad (22-5)$$

Where $[A]_0$ is the initial concentration of reactant A and $[A]$ is the concentration after time period t . Plotting $[A]$ against t gives a straight line, whose slope and y-intercept are $-k$ and $[A]_0$, respectively.

2. First order reaction

If the reaction is first order with respect to A, then the rate law equation is

$$\text{rate} = \frac{-d[A]}{dt} = k[A] \quad (22-6)$$

Integrating this, then

$$\ln[A] = -kt + \ln[A]_0 \quad (22-7)$$

Plotting $\ln[A]$ versus time t gives a straight line whose slope and y-intercept are $-k$ and $\ln[A]_0$, respectively.

3. Second order reaction

If the reaction is second order with respect to A, the rate law equation is

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^2 \quad (22-8)$$

Integrating this expression, then

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (22-9)$$

Plotting $1/[A]$ versus t gives a straight line whose slope and y-intercept are k and $1/[A]_0$, respectively.

Therefore, by determining how the concentration of A varies with time for a particular reaction, and plotting the graphs of $[A]$, $\ln[A]$ and $1/[A]$ against t to see which one gives a straight line, we can deduce the reaction order. The advantage of the graphical method is that we do not need to vary the initial concentration of reactants. An experiment can be carried out with an arbitrary initial concentration to determine the reaction order.

When the rate of a particular reaction is a function of concentrations of two or more reactants, we can still use the graphical method to find the reaction order with respect to each reactant. When designing the experiment for such a reaction, we set initial concentrations of other reactants much higher than the initial concentration of

the analyte. Hence the change in concentration of the other reactants is very small. We can therefore assume that in the reaction process, concentrations of other reactants are constant, and the rate depends only on the concentration of the analyte. The reaction order with respect to the particular reactant can thus be determined by the graphical method. If the reaction order of the investigated reactant is first order, it is addressed pseudo-first order reaction.

Hence, in the experiment we will determine the reaction order of $S_2O_8^{2-}$ by the graphical method. In each of the tests (refer to Table 22-1), the concentration of two reactants, $S_2O_8^{2-}$ and I^- , is kept constant. However, different amounts of the timing reagent $S_2O_3^{2-}$ are added to determine the changes in $[S_2O_8^{2-}]$ over different intervals of time (Δt). The reaction order and rate constant can then be found by plotting suitable graphs. In this part, we will only investigate the reaction order with respect to the reactant $S_2O_8^{2-}$. The amounts of reactants are designed such that $[I^-]$ is much greater than $[S_2O_8^{2-}]$, and $[I^-]$ is assumed to be constant throughout the reaction process.

III. Activation energy

For most chemical reactions, the reaction rate increases with increasing temperature, since a higher temperature results in a greater rate constant. In 1888, the Swedish chemist S. Arrhenius postulated that reactants require a minimum energy to pass over an energy barrier to form products. This minimum energy is called the activation energy. When the reaction temperature increases, the fraction of particles having enough energy to overcome the activation energy also increases, resulting in a faster rate, or a larger value of the rate constant. The rate constant k is related to the Kelvin temperature T by the expression shown as equation 22-10, which is known as Arrhenius equation.

$$k = Ae^{-E_a/RT} \quad (22-10)$$

where k : rate constant T : absolute temperature (K)
 A : Arrhenius constant R : gas constant, 8.314 (J/mol-K)
 E_a : activation energy e : natural logarithm base

Since A is a constant, then expressions for k as a function of T is derived (22-11).

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A \quad (22-11)$$

A plot of $\ln k$ (or $2.303 \log k$) versus $1/T$ should therefore be linear, with a slope equal to $-E_a/R$.

In the second part of the experiment, we will measure the time taken for color change (Δt) when the concentrations of reactants are constant but reaction temperature is varied. In this experiment, rate of reaction is inversely proportional to Δt . Hence

rate constant is also inversely proportional to Δt :

$$k = \frac{c}{\Delta t} \quad (22-12)$$

where k is rate constant, Δt is reaction time, and c is a constant. Hence

$$\ln k = \ln c + \ln\left(\frac{1}{\Delta t}\right) \quad (22-13)$$

Substituting this into the Arrhenius equation (22-10), we get

$$\ln c + \ln\left(\frac{1}{\Delta t}\right) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A \quad (22-14)$$

$$\ln\left(\frac{1}{\Delta t}\right) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A - \ln c \quad (22-15)$$

Therefore, plotting $\ln(1/\Delta t)$ against $1/T$ will give a straight line whose slope is $-E_a/R$. The activation energy can be calculated from this value.

IV. Catalyst and reaction rate

In the third part of this experiment, we are going to investigate how the addition of catalyst CuSO_4 into the reaction affecting the reaction rate.

Apparatus

Stirrer/hot plate, magnetic stirring bar, graduated pipet (10 mL, 2), pipet filler, Erlenmeyer flask (50 mL, 10), cork stopper (6), beaker (100 mL, 2), timer, thermometer, and Styrofoam bowl (for ice-water bath).

Chemicals

1.0 M Sodium iodide, NaI

0.15 M Potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$

0.20 M Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$

2% Starch solution

0.020 M Copper(II) sulfate, CuSO_4

Procedure

I. The integrated rate law

1. Wash ten 50 mL Erlenmeyer flasks. Dry them in the oven and allow to cool to room temperature. Label the flasks and fill them with accurately measured reagents according to Table 22-1.
2. Use dispenser to transfer accurately 5.0 mL of 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ solution to flask No. 1 and start timing. Immediately stopper the flask and swirl the solution continually to ensure even mixing of reagents.

- Stop timing when the color of the solution changes. Record the reaction time.
- Repeat steps 1~3; add 5.0 mL of 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ into flasks No. 2, 3, 4, 5, and 6. Determine Δt of each trial.
Note: $\text{K}_2\text{S}_2\text{O}_8$ solution can be added to the flasks at 1 min or 30 s intervals; carry out the reactions in a series.
- Measure the temperature of the No.5 solution before and after reaction.

Table 22-1 Reagents' volumes for integrated rate law

Trial number	2% starch (mL)	1.0 M NaI (mL)	0.20 M $\text{Na}_2\text{S}_2\text{O}_3$ (mL)	DI water (mL)
1	1.00	5.00	5.50	1.50
2	1.00	5.00	4.50	2.50
3	1.00	5.00	3.50	3.50
4	1.00	5.00	2.50	4.50
*5	1.00	5.00	1.50	5.50
6	1.00	5.00	0.50	6.50

II. Activation energy

- Prepare two dry and clean 50 mL Erlenmeyer flasks. According to trial No. 5 in Table 22-1, measure and transfer the various reagents into the flasks.
- Fill the Styrofoam bowl with ice and some water. Put one of the flasks in the ice-water bath and allow it to reach thermal equilibrium. Measure and record the equilibrium temperature of the solution. Add 5.0 mL of 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ to the flask and start timing. Stir the solution with a magnetic stirrer continually to ensure even mixing. Monitor the temperature of solution during the reaction.
Note: It may take 10~15 min for solution to react and change colors. During the reaction, continually observe the temperature and add ice to maintain the temperature.
- Repeat step 7, replacing the ice-water bath with a warm water bath (ca. 40°C) in a glass beaker without a magnetic stirrer.

Note: The temperature of the warm water bath needs to be just higher than room temperature and keep constant. It is not necessary to adjust the temperature to exactly 40°C, but the actual temperature needs to be recorded.

III. Catalyst and reaction rate

- According to trial No. 5 in Table 22-1, measure and transfer the various reagents into the flask. Record the temperature of the solution.
- Add 2 drops of 0.020 M CuSO_4 , and 5.0 mL of 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ as the last reagent. Start timing and mix the solution thoroughly. Compare the time taken for color-change with that of trial No. 5 without adding Cu^{2+} ion.

References

1. Dept. of Chemistry, U. of Illinois at Urbana-Champaign *General Chemistry Experiments, Chemistry 102*; Stipes Publishing Co., 1991.
2. Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*; 5th ed., Saunders College Publishing: Chicago, 1988; pp 124-130.

Experimental Data Sheet and Calculation

1. The integrated rate law

(1) Determination of the reaction time at room temperature

Trial No.	2% starch (mL)	1.0 M NaI (mL)	0.20 M Na₂S₂O₃ (mL)	DI water (mL)	0.15 M K ₂ S ₂ O ₈ (mL)	No. 5 temp.: _____ Reaction time (Δt, s)
1	1.0	5.0	5.5	1.5	5.0	
2	1.0	5.0	4.5	2.5	5.0	
3	1.0	5.0	3.5	3.5	5.0	
4	1.0	5.0	2.5	4.5	5.0	
*5	1.0	5.0	1.5	5.5	5.0	
6	1.0	5.0	0.50	6.5	5.0	

(2) The concentrations of reactants (NaI and K₂S₂O₈) are constant in the six trials.

Only the concentration of the timing reagent Na₂S₂O₃ is varied. Since $\Delta[\text{S}_2\text{O}_3^{2-}] = 2\Delta[\text{S}_2\text{O}_8^{2-}]$, we can calculate [S₂O₈²⁻] remaining in the solution after Δt, the time taken to see the color-change (the solution turns blue black when Na₂S₂O₃ is used up), by knowing the amount of Na₂S₂O₃ added:

- (a) Calculate the number of moles of S₂O₃²⁻ from the volume and concentration of Na₂S₂O₃ in each flask.
- (b) Calculate the concentration of S₂O₈²⁻ in each solution.
- (c) Use the relationship $\Delta[\text{S}_2\text{O}_3^{2-}] = 2\Delta[\text{S}_2\text{O}_8^{2-}]$ to calculate the number of moles of S₂O₈²⁻ remaining in each flask after Δt, and then calculate its concentration in molarity (M, mol/L).
- (d) Calculate ln[S₂O₈²⁻] and 1/[S₂O₈²⁻] for all six trials.
- (e) Show the steps of the calculations above and tabulate the results.

(3) Plot the graphs of [S₂O₈²⁻], ln[S₂O₈²⁻], and 1/[S₂O₈²⁻] (on the y-axis) versus Δt (on the x-axis), separately.

Note: MS-Excel or similar programs may be used to calculate, tabulate the calculation result, and plot the graph.

(4) According to the graphs, determine the reaction order with respect to K₂S₂O₈:

Order of reaction: _____

Rate constant: _____

2. Determination of activation energy

(1) Determination of the reaction time at various temperatures.

Trial	T (°C)	Δt (s)	T (K)	1/T (K ⁻¹)	ln(1/ Δt)
No. 5 in ice-water bath					
No. 5 in room temp.					
No. 5 in warm-water bath					

Note 1: Each reaction mixture contains 5.0 mL of 1.0 M NaI, 1.5 mL of 0.20 M Na₂S₂O₃, 1.0 mL 2% starch and 5.5 mL DI water. Add 5.0 mL of 0.15 M K₂S₂O₈ as the last reagent.

Note 2: Get the average value for T.

(2) Plot ln(1/ Δt) (y-axis) versus 1/T (x-axis) to obtain a least square regression line. Activation energy can then be determined from the slope of this line.

Note: MS-Excel or a similar program may be used to tabulate the data and plot the graph.

(3) Activation energy: _____

3. The effect of catalyst

(1) Determination of the reaction time with Cu²⁺ added.

Trial	0.020 M CuSO ₄	Δt (s)	T (°C)
No. 5 soln	2 drops		
No. 5 soln	0		

(2) Based on the experimental results, explain the effect of a catalyst on the reaction rate.